VERIFICATION OF TRANSLATION

I, Yasuo Yasutomi of MT-2 BLDG., 5-36, Miyahara 3-chome, Yodogawa-ku, Osaka-shi, Osaka 532-0003 JAPAN, hereby declare that I am conversant with the Japanese and English languages and that I am the translator of the documents attached and certify that to the best of my knowledge and belief the following is a true and correct English translation of the Japanese Patent Application No. 2002-303843 in the name of KANEKA CORPORATION.

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Yasuo Yasutomi

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[List of Attached Documents]

  [Document Name]   Specification 1

  [Document Name]   Abstract   1
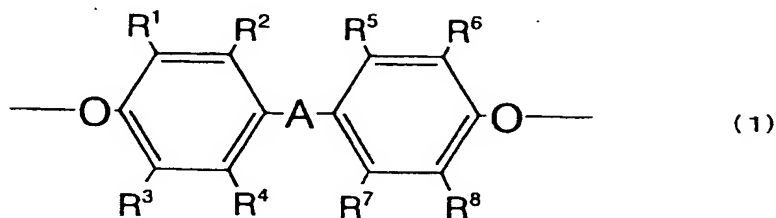
  [Necessity of Proof]   Needed

[Document Name] Specification
[Title of the Invention] POLYAMIDE RESIN COMPOSITION

[Scope of Claims for Patent]
[Claim 1] A polyamide resin composition comprising a polyamide resin, swelling mica treated with a polyether compound, and an electroconductive carbon compound, wherein the polyether compound is represented by the general formula (1):
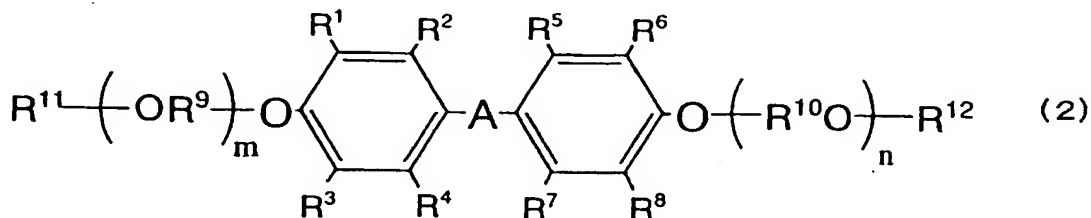[Chemical formula 1]

$$\text{---O}\underset{R^3 \quad R^4}{\overset{R^1 \quad R^2}{\bigcirc}}\text{-A-}\underset{R^7 \quad R^8}{\overset{R^5 \quad R^6}{\bigcirc}}\text{O---} \qquad (1)$$

(wherein -A- represents -O-, -S-, -SO-, -SO$_2$-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R^1 , R^2, R^3, R^4, R^5, R^6, R^7, and R^8 each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms, and the Rs may be the same or different).

[Claim 2] The polyamide resin composition of claim 1, wherein the polyether compound is represented by the general formula (2):
[Chemical formula 2]

$$R^{11}\text{---}(\text{OR}^9)_m\text{---O}\underset{R^3 \quad R^4}{\overset{R^1 \quad R^2}{\bigcirc}}\text{-A-}\underset{R^7 \quad R^8}{\overset{R^5 \quad R^6}{\bigcirc}}\text{O---}(R^{10}O)_n\text{---}R^{12} \qquad (2)$$

(wherein -A- represents -O-, -S-, -SO-, -SO$_2$-, -CO-, an alkylene

group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms,; R^9 and R^{10} each represent a divalent hydrocarbon group having 1 to 5 carbon atoms; R^{11} and R^{12} each represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms, and the Rs may be the same or different; and m and n each represent the number of oxyalkylene repeating units; and $2 \leq m+n \leq 50$).

[Claim 3] The polyamide resin composition of claim 1 or 2, prepared by mixing the polyamide resin, the swelling mica treated with a polyether compound, and the electroconductive carbon compound.

[Claim 4] The polyamide resin composition of claim 1, 2 or 3, wherein the carbon compound is in the form of particles.

[Claim 5] The polyamide resin composition of claim 1, 2 or 3, wherein the carbon compound is fibrous.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Pertains]

The present invention relates to polyamide resin compositions containing polyamide resins, swelling mica treated with polyether compounds, and electroconductive carbon black.

[Background Art]

[0002]

Recent development in electronic technology has led to an increase in demand for electrostatic recording sheets; housings for electronic devices; electrostatic containers; electrostatic films; floor covering, wall materials, and partitions for clean rooms; covering materials for electronic devices; and magazines for ICs and the like. The materials used therefor must satisfy the required dimensional accuracy, low warpage, surface quality, high stiffness, and heat resistance.

Furthermore, since polyamide resins have excellent heat resistance, mechanical properties, and the like, they are used in many industrial applications, such as materials for injection molding, sheets, and films. However, polyamide
5   resins readily become electrostatically charged and thus cannot be directly applied to films, sheets, and containers composed of boards because accumulation of electrostatic charge should be avoided. Accordingly, techniques of rendering electric conductivity to synthetic resins are widely employed. In
10   general, for example, carbon fibers (See Patent Documents 1 and 2) and carbon black (See Patent Documents 3 and 4) are used.
         [0003]
         However, when products are fabricated using materials containing carbon fibers for rendering conductivity, carbon
15   fibers frequently appear in the surfaces of the products. Thus, when such products are used as containers or transfer trays, the surfaced carbon fibers will damage ICs and other electronic components. Furthermore, during molding, carbon fibers align in the direction of flow, thereby generating anisotropy. This
20   leads to another problem, i.e., warpage in the molded products. When carbon black is used, inorganic fillers are used to provide stiffness and heat resistance; however, inorganic fillers decrease surface quality and cause warpage.
         [0004]
25   As is stated above, a technique that can provide conductive polyamide resin compositions having excellent heat resistance, stiffness, and surface quality while achieving low warpage has not been found so far.
         [0005]
30   [Patent Document 1] Japanese Unexamined Patent Application Publication No. 7-205310
         [0006]
     [Patent Document 2] Japanese Unexamined Patent Application Publication No. 10-237316
35   [0007]

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 11-310701

[0008]

[Patent Document 4] Japanese Unexamined Patent Application Publication No. 7-331029

[0009]

[Problem to be solved by the Invention]

An object of the present invention is to overcome the above-described problems experienced in the conventional art by providing a polyamide resin composition having excellent surface quality, low warpage, satisfactory mechanical properties, and high heat resistance.

[0010]
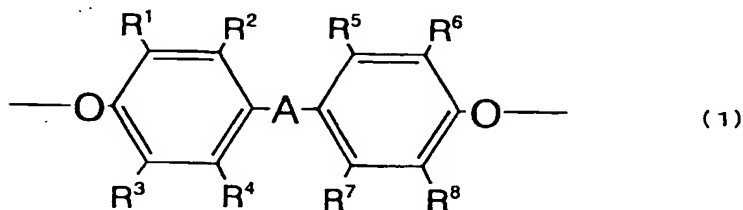
[Means for solving problem]

The present inventors have conducted extensive investigations to achieve these objects and completed the invention of an electroconductive polyamide resin composition with superior properties, by adding an electroconductive carbon black, and finely and homogeneously dispersing swelling mica treated with a particular polyether compound in a polyamide resin by extrusion.

[0011]

In particular, the first aspect of the present invention provides a polyamide resin composition comprising a polyamide resin, swelling mica treated with a polyether compound and an electroconductive carbon compound, wherein the polyether compound is represented by general formula (1):
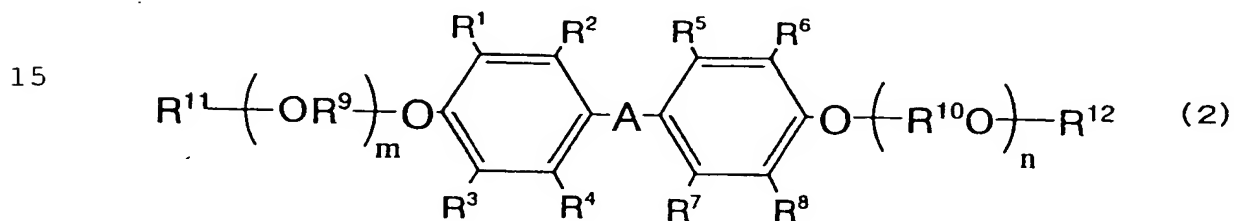
[0012]

[Chemical formula 3]

(1)

(wherein -A- represents -O-, -S-, -SO-, -SO$_2$-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R^1 , R^2, R^3, R^4, R^5, R^6, R^7, and R^8 each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms, and the Rs may be the same or different).

[0013]

In a preferred embodiment of the polyamide resin composition, the polyether compound is represented by general formula (2):

[0014]

[Chemical formula 4]

$$R^{11}{-}{\left(OR^9\right)}_m{-}O{-}\!\!\underset{R^3\quad R^4}{\overset{R^1\quad R^2}{\bigcirc}}\!\!{-}A{-}\!\!\underset{R^7\quad R^8}{\overset{R^5\quad R^6}{\bigcirc}}\!\!{-}O{-}{\left(R^{10}O\right)}_n{-}R^{12} \quad (2)$$

(wherein -A- represents -O-, -S-, -SO-, -SO$_2$-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R^1, R^2, R^3 , R^4, R^5, R^6, R^7, and R^8 each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms,; R^9 and R^{10} each represent a divalent hydrocarbon group having 1 to 5 carbon atoms; R^{11} and R^{12} each represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms, and the Rs may be the same or different; and m and n each represent the number of oxyalkylene repeating units; and 2 ≤ m+n ≤ 50).

[0015]

In a preferred embodiment of the polyamide resin composition, the polyamide resin composition is prepared by mixing the polyamide resin, and the swelling mica treated with a particular polyether compound, and the electrically conductive carbon black.

[0016]

In another preferred embodiment of the polyamide resin composition, the carbon compound is in the form of particles.

[0017]

5　　　In another preferred embodiment of the polyamide resin composition, the carbon compound is fibrous.

[0018]

[Mode for Carrying Out the Invention]

In the present invention, polyamide resins used are

10　polymers that contain amide bonds (-NHCO-) in the main chains and melt by heating.　Examples of such polyamide resins include polycaproamide (nylon 6), polytetramethylene adipamide (nylon 46), polyhexamethylene adipamide (nylon 66), polyhexamethylene sebacamide (nylon 610), polyhexamethylene

15　dodecamide (nylon 612), polyundecamethylene adipamide (nylon 116), polyundecanamide (nylon 11), polydodecaneamide (nylon 12), polytrimethylhexamethylene terephthalamide (nylon TMHT), polyhexamethylene isophthalamide (nylon 6I), polyhexamethylene terephthal/isophthalamide (nylon 6T/6I),

20　polybis(4-aminocyclohexyl)methane dodecamide (nylon PACM12), polybis(3-methyl-4-aminocyclohexyl)methane dodecamide (nylondimethyl PACM12), polymetaxylylene adipamide (nylon MXD6), polyundecamethylene terephthalamide (nylon 11T), polyundecamethylene hexahydroterephthalamide (nylon 11T(H)),

25　and copolymers and mixtures of these polyamides.　Among these, nylon 6, nylon 46, nylon 66, nylon MXD6, nylon 11, nylon 12, and copolymers and mixtures of these polyamides are preferred. Aromatic polyamide resins may be used.　The molecular weights of these polyamide resins are not particularly limited.　In

30　general, polyamide resins having relative viscosities of 0.5 to 5.0 measured in conc. H_2SO_4 at 25°C are preferred.

[0019]

These polyamide resins may be used alone.　Alternatively, two or more of these polyamide resins having different

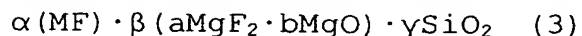35　compositions or components and/or different relative

viscosities may be used.

[0020]

Among these, Nylon 6, nylon 66, nylon 46, and nylon MXD6 are more preferable from the standpoints of strength, modulus of elasticity, cost, and the like.

[0021]

The swelling fluorinated mica used in the present invention may be produced by heating a mixture of talc and a silicofluoride or fluoride of sodium and/or lithium. A specific production method is disclosed in Japanese Unexamined Patent Application Publication No. 2-149415. In this method, talc is subjected to intercalation of a sodium ion and/or a lithium ion to obtain swelling mica. In particular, talc is mixed with a silicofluoride and/or a fluoride, and the resulting mixture is treated at approximately 700°C to 1,200°C to obtain swelling mica. In the present invention, swelling fluorinated mica produced by this method is particularly preferable. In order to obtain swelling mica, sodium or lithium must be the metal contained in the silicofluoride or the fluoride. These may be used alone or in combination. The total content or the content of the silicofluoride and/or the fluoride mixed with talc is preferably 10 to 35 percent by weight of the entirety of the mixture. If the content is out of the range, yield of the swelling mica may be decreased. The swelling mica produced by the above-described method has a structure represented by general formula (3) below:

$$\alpha(MF) \cdot \beta(aMgF_2 \cdot bMgO) \cdot \gamma SiO_2 \quad (3)$$

(wherein M represents sodium or lithium; α, β, γ, a, and b each represent a coefficient; $0.1 \leq a \leq 2$; $2 \leq \beta \leq 3.5$; $3 \leq \gamma \leq 4$; $0 \leq a \leq 1$; $0 \leq b \leq 1$; and a+b=1).

Alternatively, it is possible to add a small amount of alumina (Al_2O_3) during the process of producing the swelling mica used in the present invention so as to control the swelling property of the resulting swelling mica.
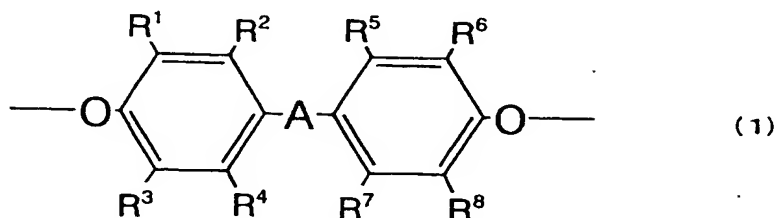
[0022]

These are substances having such properties that swell in water, polar solvents miscible with water at arbitrary ratios, and mixed solvents containing water and any of these polar solvents. In this invention, "swelling property" refers to the property of mica to absorb polar molecules between the layers, thereby increasing the interlayer distance or to extensively swell, thus leading to cleaving. Examples of the swelling mica include lithium taeniolite, sodium taeniolite, lithium tetrasilicic mica, and sodium tetrasilicic mica, or substitution products thereof, derivatives thereof, or mixtures thereof. The swelling mica in an initial aggregation state, i.e., before swelling, has a basal-plane spacing of approximately 10 to 17 Å and an average particle diameter of approximately 1,000 to 1,000,000 Å.

[0023]

The polyether compound used in the present invention includes a structure represented by general formula (1) in the side chain and/or the main chain of a polyoxyalkylene compound such as polyoxyethylene or a polyoxyethylene-polyoxypropylene copolymer:

[0024]

[Chemical formula 5]

(1)

(wherein -A- represents -O-, -S-, -SO-, -SO$_2$-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms, and the Rs may be the same or different).

[0025]

Among the above-described polyether compounds, those having a structure represented by general formula (2) below are preferred from the standpoints of thermal stability, dispersibility of the lamellar substance, and ready availability:

[0026]

[Chemical formula 6]

$$R^{11}\text{---}\left(OR^9\right)_m\text{---}O\underset{\underset{R^3 \quad R^4}{}}{\overset{\overset{R^1 \quad R^2}{}}{\bigcirc}}\text{---}A\text{---}\underset{\underset{R^7 \quad R^8}{}}{\overset{\overset{R^5 \quad R^6}{}}{\bigcirc}}O\text{---}\left(R^{10}O\right)_n\text{---}R^{12} \qquad (2)$$
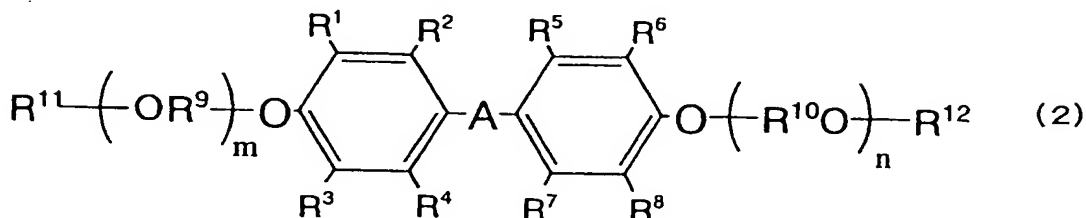
(wherein -A- represents -O-, -S-, -SO-, -SO$_2$-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms,; R^9 and R^{10} each represent a divalent hydrocarbon group having 1 to 5 carbon atoms; R^{11} and R^{12} each represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms, and the Rs may be the same or different; and m and n each represent the number of oxyalkylene repeating units; and 2 ≤ m+n ≤ 50).

[0027]

The above-described polyether compounds may contain a functional group or groups. The functional group may be any one provided that it does not adversely affect the polyamide resin or swelling mica. Examples of the substituents include saturated or unsaturated monovalent or multivalent aliphatic hydrocarbon groups; groups containing ester bonds; an epoxy group; an amino group; a carboxyl group; carbonyl-terminated groups; an amide group; a mercapto group; groups containing

sulfonyl bonds; groups containing sulfinyl bonds; a nitro group; a nitroso group; a nitrile group; halogen atoms; and a hydroxyl group. The polyether compounds may be substituted with one of these or two or more of these.

5   [0028]

The content of the substituent in the polyether compound is not particularly limited as long as the polyether compound is soluble in water or a polar solvent containing water. In particular, the solubility of the polyether compound is

10   preferably 1 g or more, more preferably 2 g or more, yet more preferably 5 g or more, still more preferably 10 g or more, and most preferably 20 g or more in 100 g of water at room temperature.

[0029]

15   Examples of the polar solvent include alcohols such as methanol, ethanol, and isopropanol; glycols such as ethylene glycol, propylene glycol, and 1,4-butanediol; ketones such as acetone and methyl ethyl ketone; ethers such as diethyl ether and tetrahydrofuran; amide compounds such as

20   N,N-dimethylformamide and N,N-dimethylacetamide; and other solvents such as pyridine; dimethylsulfoxide; and N-methylpyrrolidone. Carbonic acid diesters such as dimethyl carbonate and diethyl carbonate may also be used. These polar solvents may be used alone or in combination.

25   [0030]

The amount of the polyether compound used can be adjusted to enhance the affinity between the swelling mica and the polyamide resin and to sufficiently improve the dispersibility of the swelling mica in the polyamide resin composition. If

30   necessary, two or more polyether compounds having different functional groups may be used simultaneously. Thus, the amount of the polyether compound to be formulated cannot be limited by specific numerical values; however, the lower limit of the amount of the polyether compound to 100 parts by weight of the

35   swelling mica is preferably 1 part by weight, more preferably

2 parts by weight, and most preferably 5 parts by weight. If the lower limit of the amount of the polyether compound is below 1 part by weight, fine dispersion of the swelling mica tends to be insufficient. The upper limit is not particularly limited,

5 but it is no need to use more than 200 parts by weight to 100 parts by weight of the swelling mica because fine dispersion of the swelling mica also tends to be insufficient when the amount exceeds 200 parts by weight.

[0031]

10 In the present invention, the process for treating the swelling mica with the polyether compound is not particularly limited. For example, the method described below may be employed.

[0032]

15 First, swelling mica and a dispersion medium are mixed. Here, the dispersion medium is either water or a polar solvent containing water.

[0033]

The method for mixing the swelling mica and the dispersion

20 medium is not particularly limited. For example, the mixing may be performed using a conventional wet mixer. Examples of the wet mixer include high performance mixers having mixing blades rotating at high speeds; wet mills for wet-milling samples in the gaps between rotors and stators at high shear

25 rate; mechanical pulverizers for wet processes using hard media; impact pulverizers for wet processes, in which samples are collided at high speeds using jet nozzles and the like; and ultrasonic pulverizers for wet processes using ultrasonic waves. In order to achieve more efficient mixing, the number of

30 revolutions for mixing may be increased to 1,000 rpm or more, preferably 1,500 rpm or more, and more preferably 2,000 rpm or more. Alternatively, the shear rate may be increased to 500 (1/s) or more, preferably 1,000 (1/s) or more, and more preferably 1,500 (1/s) or more. The upper limit of the number

35 of revolutions is approximately 25,000 rpm, and the upper limit

of the shear rate is approximately 500,000 (1/s). Since mixing or application of shear beyond the upper limits does not improve the mixing efficiency, there is no need to conduct mixing beyond the upper limits. Moreover, the time taken for mixing is preferably 10 minutes or more. Next, the polyether compound is added, and the mixing is further continued to thoroughly mix the components.

[0034]

The mixing may be performed with a conventional mixer. Mixers are classified into batch mixers and continuous mixers. Examples of the batch mixers include open-type rollers, and closed-type banbury mixers. Examples of the continuous mixers include single-shaft rotor mixers, twin-shaft rotor mixers, single-shaft screw mixers, twin-shaft screw mixers, multishaft screw mixers, and kneader-type mixers. After the mixing, drying and, if necessary, powdering may be performed.

[0035]

The lower limit of the ash content in the polyamide resin composition derived from the swelling mica is typically adjusted to 0.5 percent by weight and preferably 1.0 percent by weight. The upper limit of the ash content is typically adjusted to 50 percent by weight, preferably 40 percent by weight, and more preferably 30 percent by weight. If the ash content is below 0.5 percent by weight, improvement of mechanical properties or warpage reduction may be insufficient, and the upper limit exceeds 50 percent by weight, surface appearance of the resulting product may be deteriorated.

[0036]

The structure of the swelling mica dispersed in the polyamide resin composition of the present invention is completely different from the structure of the swelling mica before use. Whereas the swelling mica before the use has micrometer-order aggregated structures consisting of many thin layers, the swelling mica after treatment with the polyether forms independent fine segments as a result of cleaving of the

layers. Consequently, the swelling mica becomes dispersed in the polyamide resin composition by forming significantly fine lamellae independent from one another. The number thereof is markedly larger than the number of the swelling mica particles before the use. Such a state of dispersion of the lamellar swelling mica can be expressed by the equivalent circular diameter [D], the aspect ratio (layer length/layer thickness), the number of dispersed particles, the maximum layer thickness, and the average layer thickness.

[0037]

The equivalent circular diameter [D] is defined as the diameter of a circle having the equivalent area as the particle of the swelling mica dispersed in various shapes observed in a micrograph or the like. Of the swelling mica particles dispersed in the polyamide resin composition, those having an equivalent circular diameter [D] of 3000 Å or less is preferably contained in an amount of 20% or more, more preferably 35% or more, yet more preferably 50% or more, and most preferably 65% or more. If the proportion of the swelling mica with the equivalent circular diameter [D] of 3000 Å or less is lower than 20%, improvement of the mechanical properties of the polyamide resin composition and the warpage reduction may be insufficient. In the polyamide resin composition of the present invention, the average of the equivalent circular diameters [D] of the swelling mica is preferably 5,000 Å or less, more preferably 4,500 Å or less, yet more preferably 4,000 Å or less, and most preferably 3,500 Å or less. If the average of the equivalent circular diameters [D] is larger than 5,000 Å, improvement of the mechanical properties of the polyamide resin composition, warpage reduction may be insufficient, and surface appearance of the resulting product may be deteriorated. The lower limit is not particularly limited. Since no improvement occurs below 100 Å, there is no need to adjust the average equivalent circular diameter to below 100 Å.

[0038]

The equivalent circular diameter [D] may be determined by obtaining a picture of a melt-mixed material, an injection-molded product, or a heat-pressed product using a microscope or the like, arbitrarily selecting from the picture

5   a particular region containing 100 or more of layers of swelling mica, and performing image processing using an image processor or the like so as to allow computer processing for quantitative determination.

[0039]

10   The average aspect ratio is defined as the number-average of the ratio, layer length/layer thickness, of the swelling mica dispersed in the resin. The lower limit of the average aspect ratio of the swelling mica in the polyamide resin composition of the present invention is preferably 10, more preferably 20,

15   and most preferably 30. If the aspect ratio is lower than 10, improving effect of mechanical properties and the like of the polyamide resin composition of the present invention may be insufficient. Since the effect does not change at average aspect ratios exceeding 300, there is no need to increase the

20   average aspect ratio to beyond 300.

[0040]

Here, the number of the dispersed particles per unit weight ratio of the swelling mica found in an area of 100 μm^2 of the polyamide resin composition is defined as [N] value. The

25   [N] value of the swelling mica in the polyamide resin composition of the present invention is preferably 30 or more, more preferably 45 or more, and most preferably 60 or more. The upper limit is not particularly limited. However, the effect does not change at [N] values exceeding about 1,000; thus, there

30   is no need to increase the [N] value to over 1,000. For example, [N] values are determined as follows: From a polyamide resin composition, a very thin slice approximately 50 to 100 μm in thickness is cut. A picture of the slice is taken by transmission electron microscopy (TEM) or the like, and the

35   number of particles of the swelling mica found in a desired 100

μm^2 region in the picture is counted. The number is divided by the weight ratio of the swelling mica used. Alternatively, the [N] value can be determined by selecting a desired region (whose area is measured in advance) containing more than 100

5 particles from a TEM micrograph, dividing the number of the swelling mica particles in that region by the weight ratio of the swelling mica used, and converting the obtained value to a 100 μm^2 equivalent so as to define this converted value as the [N] value. Thus, the [N] values can be determined by using

10 TEM micrographs or the like of the polyamide resin composition.

[0041]

The average layer thickness is defined as the number-average value of the thickness of the layers of the dispersed lamellar swelling mica. Here, the upper limit of the

15 average thickness of the swelling mica in the polyamide resin composition is preferably 500 Å or less, more preferably, 450 Å or less, and most preferably 400 Å or less. If the average layer thickness is larger than 500 Å, improvement of the mechanical properties and the like of the polyamide resin

20 composition may be insufficient. The lower limit of the average layer thickness is not particularly limited. However, since no change in effects occurs below 50 Å, there is no need to reduce the average layer thickness to 50 Å or less.

[0042]

25 The maximum layer thickness is defined as the maximum thickness of the layers of the lamellar swelling mica dispersed in the polyamide resin composition of the present invention. Here, the upper limit of the maximum layer thickness is preferably 2,000 Å or less, more preferably 1,800 Å or less,

30 and most preferably 1,500 Å or less. If the maximum layer thickness is larger than 2,000 Å, mechanical properties of the polyamide resin composition and surface appearance of the resulting product may be deteriorated. The lower limit of the maximum layer thickness of the swelling mica is not particularly

35 limited but is preferably at least 100 Å , more preferably at

least 150 Å, and most preferably at least 200 Å.

[0043]

The layer thickness and the layer length can be determined from a micrograph or the like of a film prepared by
5   heat-press-molding or draw-molding a polyamide resin composition of the present invention melted by heating or from a picture of a thin product prepared by injection-molding using a molten resin. In particular, assume that a film prepared as above or an injection-molded thin, flat specimen having a
10   thickness of approximately 0.5 to 2 mm is placed on the X-Y plane. From this film or the specimen, a very thin slice having a thickness of approximately 50 to 100 μm is cut out along a plane parallel to the X-Z plane or the Y-Z plane, and this slice is observed at high magnifications of about 40,000 to 100,000 or
15   more by transmission electron microscopy or the like to determine these values. Alternatively, these values can be determined by arbitrarily selecting a region containing 100 or more particles of the swelling mica from a TEM micrograph taken as in the above and performing the image processing to allow
20   computer processing for quantitative determination. Alternatively, a ruler or the like may be used for the determination.

[0044]

The electroconductive carbon compound used in the present
25   invention is not particularly limited and may be any commercially available product other than carbon fibers. From the standpoint of the surface quality, warpage, deformation, and the like of the resulting product, the carbon compound is preferably in the form of particles or fine fibrils. Examples
30   of the electroconductive carbon compound in the form of particles include acetylene black and various furnace carbon blacks having electric conductivity. Various commercially available products may be used. An example is Ketjenblack (trade name) produced by KetjenBlack International. Examples
35   of the electroconductive carbon compound in the form of fine

fibrils include fibrous carbon compounds having a diameter of
approximately 3.5 to 75 nm, a.k.a., carbon nanotubes. Various
commercially available carbon nanotubes may be used. An
example is Hyperion (trade name) produced by Hyperion Catalysis
International. These may be used alone or in combination. The
lower limit of the amount of the electroconductive carbon
compound added to 100 parts by weight of the polyamide resin
is 0.5 parts by weight, preferably 1.0 part by weight, and more
preferably 1.5 parts by weight. If the amount is less than the
lower limit, electroconductivity may be sufficient. The upper
limit of the carbon compound added is 12 parts by weight,
preferably 11 parts by weight, and more preferably 10 parts by
weight. If the amount exceeds 12 parts by weight, pelletization
of the resin composition by extrusion may be hard to perform,
and mechanical strength of the resultant product may be reduced.

[0045]

The method for producing the polyamide resin composition
of the present invention is not particularly limited. For
example, the polyamide resin composition may be made by
melt-mixing the polyamide resin, the swelling mica treated by
the polyether compound, and the electroconductive carbon
compound using various types of conventional mixers. Examples
of the mixer include single-shaft extruders, twin-shaft
extruders, rollers, banbury mixers, and kneaders. Mixers
having high shear efficiency are particularly preferable. The
polyamide resin, the swelling mica treated with the polyether
compound, and the electroconductive carbon compound may be
simultaneously placed in the above-described mixer.
Alternatively, the polyamide resin may be melted in advance and
then melt-mixed with the swelling mica and the
electroconductive carbon compound.

[0046]

If necessary, the polyamide resin composition of the
present invention may contain polybutadiene, a
butadiene-styrene copolymer, acryl rubber, ionomer, an

ethylene-propylene copolymer, an ethylene-propylene-diene copolymer, natural rubber, chlorinated butyl rubber, an α-olefin homopolymer, a copolymer of two or more α-olefins (the copolymer may be a random copolymer, a block copolymer, a graft copolymer, or the like, or may be a mixture of these), or an impact resistance improver such as an olefin elastomer. These may be modified by an acid compound such as maleic anhydride or an epoxy compound such as glycidyl methacrylate.

[0047]

As long as the mechanical properties and the like are not adversely affected, any other thermoplastic resin or thermosetting resin may be used. Examples thereof include unsaturated polyester resins, polyester carbonate resins, liquid crystalline polyester resins, polyolefin resins, thermoplastic polyester resins, rubber polymer-reinforced styrene resins, polyphenylene sulfide resins, polyphenylene ether resins, polyacetal resins, polysulfone resins, and polyarylate resins. These may be used alone or in combination.

[0048]

Depending on the purpose, various additives, such as pigments and dyes, a heat stabilizer, an antioxidant, a UV absorber, a photostabilizer, a lubricant, a plasticizer, and an antistatic agent such as a surfactant, may be added.

[0049]

The polyamide resin composition obtained in the present invention may be used for producing products prepared by injection molding. The resulting molded product has electric conductivity and antistatic property and suffers little from anisotropy that leads to mold shrinkage. Thus, warpage is small even when a complex-shaped product is made by injection molding. Moreover, the stiffness and the heat resistance are excellent without lowering the surface quality of the polyamide resin. Thus, the composition is suitable for use in electrostatic recording sheets; housings for electronic devices; electrostatic containers; electrostatic films; floor

coverings, wall materials, and partitions for clean rooms;
covering materials for electronic devices; magazines for ICs
and the like; and antistatic transfer trays for other electronic
components, for example.

5   [0050]

Alternatively, the polyamide resin composition of the
present invention may be molded by heat-press molding and can
be used in blow molding. The resulting product has excellent
appearance, satisfactory mechanical properties, and high
10 resistance to thermal deformation. Thus, for example, the
composition is suitable for use in automobile parts, parts for
home appliances, domestic housewares, wrapping materials, and
other general industrial materials.

[0051]

15 [EXAMPLES]

The present invention will now be described in detail with
reference to the examples below; however, the present invention
is not limited to these examples.

[0052]

20 Below is a summary list of the primary materials used in
EXAMPLES and COMPARATIVE EXAMPLES. Note that these materials
were not purified unless otherwise noted.

(Materials)
25 - Polyamide resin A (Nylon 6): Unitika Nylon 6 A1030BRL (product
of Unitika Ltd.)
- Polyamide resin B (Nylon 66): Unitika Nylon 66 A125N (product
of Unitika Ltd.)
- Polyamide resin C (Nylon 46): Stanyl TS300 (product of
30 DSM-JSR)
- Polyamide resin D (Nylon MXD6): Reny 6002 (product of Asahi
Kasei Corporation)
- Swelling mica E: Somasif ME100 (product of Co-op Chemical Co.,
Ltd.)
35 - Polyether compound G: BISOL 18EN (product of Toho Chemical

Industry Co., Ltd.)
- Polyether compound H: BISOL 20PN (product of Toho Chemical
Industry Co., Ltd.)
- Electroconductive carbon compound I: Ketjenblack (product of
5 KetjenBlack International)
- Electroconductive Carbon compound J: master batch pellets
containing PA6 and a fibril carbon material dispersed in PA6
at a concentration of 20%, product name MB4020-00 (product of
Hyperion Catalysis International)
10 - Electroconductive carbon compound K: master batch pellets
containing PA66 and a fibrous carbon material dispersed in PA66
in a concentration of 20%, product name MB4620-00 (product of
Hyperion Catalysis International)

15 (Determining Dispersion State)
Dispersion state was determined using an ultrathin
section 50 to 100 μm in thickness obtained by a frozen section
technique. The section was observed with a transmission
electron microscope (JEM-1200EX, product of JEOL) with an
20 accelerating voltage of 80 kV at a magnification of 40,000 to
1,000,000 to obtain a microgram of the dispersion state of
swelling mica. From this TEM micrograph, a region containing
100 or more of dispersed particles was arbitrarily selected.
The layer thickness, the layer length, and the number of
25 particles ([N] values) were determined either manually with a
graduated ruler or by processing the microgram with Image
Analyzer PIAS III produced by Inter Quest Co., Ltd.
[0053]
The equivalent circular diameter [D] was determined with
30 Image Analyzer PIAS III produced by Inter Quest Co., Ltd.
[0054]
The [N] values were determined as follows. First, the
number of particles of the swelling mica present in the selected
region in the TEM micrograph was determined. The ash content
35 of the resin composition derived from the swelling mica was

separately determined. The number of the particles was divided by the ash content and the result was converted to a number per 100 μm^2 area. The number-average value of the layer thickness of the swelling mica was assumed as the average layer thickness;

5   and the maximum value among the layer thickness of the swelling mica was assumed as the maximum layer thickness. A sample containing large dispersed particles and thus not suitable for observation by TEM was examined using an optical microscope (Optical microscope BH-2 produced by Olympus Optical Co., Ltd.),

10   and the [N] values were determined as is described above. Where required, a sample was melted at 250°C to 270°C using Hotstage THM 600 produced by Linkam Scientific Instruments Ltd., and the state of the dispersed particle was observed in a molten state. The number-average value of the ratios of layer length to layer

15   thickness of the individual swelling mica particles was assumed as the average aspect ratio. For dispersed particles that were not lamellar, the aspect ratio was determined as the ratio, major axis/minor axis. Here, a "major axis" is the long side of a hypothetic rectangle having the minimum area among

20   hypothetic rectangles circumscribed with a target particle in a micrograph, and a "minor axis" is the short side of this hypothetic rectangle.

(Flexural Properties)

25   The polyamide resin composition of the present invention was dried (90°C, 10 hours). Using an injection molding machine operating at a clamping pressure of 75 tons, a specimen having dimensions of approximately 10 x 100 x 6 mm was formed by injection molding at a resin temperature in the range of 240°C

30   to 300°C (Nylon 6: 240°C, Nylon 66: 260°C, Nylon MXD6: 280°C, Nylon 46: 300°C). The flexural strength and the flexural elastic modulus of the specimen were measured according to ASTM D-790.

35   (Deflection Temperature Under Load)

The deflection temperature under load was determined according to ASTM D-648 under a load of 1.86 MPa by using the same type of specimen used in determining the flexural properties.

5

(Warpage)

The polyamide resin composition of the present invention was dried (90°C, 10 hours). A tabular specimen having dimensions of approximately 120 x 120 x 1 mm was formed by injection molding at a resin temperature in the range of 240°C to 300°C (Nylon 6: 240°C., Nylon 66: 260°C, Nylon MXD6: 280°C, Nylon 46: 300°C). The tabular specimen was placed on a flat surface, and one of the four corners was held down. Of the remaining three corners, one most distant from the flat surface was determined by measuring the distance with a slide caliper. The same was repeated for every corner, and the obtained warpages were averaged.

(Mold Shrinkage Rate)

The polyamide resin composition of the present invention was dried (90°C, 10 hours). A tabular specimen having dimensions of approximately 120 x 120 x 2 mm was formed by injection molding at a resin temperature in the range of 240°C to 300°C (Nylon 6: 240°C, Nylon 66: 260°C, Nylon MXD6: 280°C, Nylon 46: 300°C). The mold shrinkage rate was determined by the following equation. In the table below, MD denotes the direction of the resin flow, and TD denotes a direction orthogonal to the resin flow.

Mold shrinkage rate (%)
= (size of die-observed size of molded product)/(size of die) x 100

(Centerline Average Roughness)

The centerline average roughness was determined with

surface analyzer Surfcom 1500A produced by Tokyo Seimitsu Co., Ltd., using the same type of above specimen u.

(Volume Resistivity)

The volume resistivity was determined with resistance meter R8340A produced by Advantest Corporation using the same type of specimen used in determining mold shrinkage rate. The volume resistivity was measured after the specimen was allowed to stand at 25°C and 50% RH for 24 hours.

(Ash Content)

The ash content of the polyamide resin composition derived from the swelling mica was determined according to JIS K 7052.

[0055]

(SYNTHETIC EXAMPLE 1)

Ion-exchange water, polyether compound G, polyether compound G;H, and swelling mica E at the weight ratios set forth in Table 1 were mixed for 15 to 30 minutes. The mixture was then dried and powdered to prepare swelling mica (L-1 and L-2) treated with the polyether compounds.

[0056]

[Table 1]

	Clay L-1	Clay L-2
Water	100	100
Swelling mica E	8	8
Polyether compound G	1.6	
Polyether compound H		4

(unit: parts by weight)

(EXAMPLES 1 to 6)

Polyamide A, the swelling mica prepared in SYNTHETIC EXAMPLE 1 (L-1 and L-2), and electroconductive carbon compound I or electroconductive carbon compound J at the weight ratios
5 set forth in Table 2 were melt-mixed
using a twin shaft extruder (TEX 44 produced by Japan Steel Works, Ltd.) while adjusting the temperature to the dies to 220°C to 250°C from the initial stage of the mixing. Evaluation of the resulting polyamide resin compositions was carried out. The
10 results are shown in Table 2.

[0057]

25

[Table 2]

		EXAMPLES					
		1	2	3	4	5	6
Polyamide resin A	Parts by weight	100	100	100	100	91	91
Clay L-1		6.6	6.6	13.6		6.6	13.6
Clay L-2					18		
Carbon compound I		3.5	4.5	4.5	4.5		
Carbon compound J						9	9
Ash content	wt%	5.0	5.0	9.9	10.2	5.0	10.1
Ratio of [D] ≤ 3,000 Å	%	93	92	90	81	93	89
Average [D]	Å	980	990	1040	1170	990	1060
Number of dispersed particles [N]	no./wt%·100 μm²	146	144	135	113	145	130
Average aspect ratio	-	125	125	140	108	122	135
Average layer thickness	Å	80	80	85	95	75	85
Maximum layer thickness	Å	300	310	330	390	315	330
Flexural elastic modulus	MPa	4200	4150	5450	5100	4060	5400
Flexural strength	MPa	105	104	130	130	104	128
Deflection temperature under load	°C	130	131	145	139	129	143
Volume resistivity	Ω·cm	1.9×10^{11}	3.2×10^5	9.4×10^4	7.5×10^5	4.2×10^8	2.1×10^8
Warpage	mm	1.6	1.5	1.3	1.6	1.6	1.3
Mold shrinkage rate MD	%	0.67	0.65	0.44	0.47	0.66	0.45
TD		0.69	0.68	0.49	0.53	0.69	0.49
Centerline average roughness	nm	2.5	2.6	4.0	4.0	2.0	3.4

(COMPARATIVE EXAMPLES 1 to 5)

　　　Polyamide A, talc, mica, a glass fiber or electroconductive carbon compound at the weight ratios set forth in Table 3 were melt-mixed as in EXAMPLE 1 to prepare polyamide resin compositions. Evaluation of them was carried out. The results are shown in Table 3.

　　　[0058]

[Table 3]

		COMPARATIVE EXAMPLES				
		1	2	3	4	5
Polyamide A	Parts by weight	100	100	100	100	100
Talc				11		
Mica					11	
Glass fibers						11
Carbon compound I			4.5	4.5	4.5	4.5
Ash content	wt%	0.0	0.0	10.0	9.9	9.9
Ratio of [D] ≤ 3,000 Å	%	Not measured	Not measured	0	0	Not measured
Average [D]	Å	Not measured	Not measured	24200	25800	Not measured
Number of dispersed particles [N]	no./wt% ·100 μm^2	Not measured	Not measured	5	2	Not measured
Average aspect ratio	-	Not measured	Not measured	1.5 (*1)	1.5 (*1)	Not measured
Average layer thickness	Å	Not measured	Not measured	App. 30,000 (*2)	App. 30,000 (*2)	Not measured
Maximum layer thickness	Å	Not measured	Not measured	App. 900,000 (*3)	App. 900,000 (*3)	Not measured
Flexural elastic modulus	MPa	2700	2730	3010	4250	5400
Flexural strength	MPa	96	96	95	120	130
Deflection temperature under load	°C	69	70	72	90	148
Volume resistivity	Ω·cm	7.0×10^{14}	9.5×10^5	7.1×10^5	4.4×10^5	2.1×10^5
Warpage	mm	8.1	8.0	7.8	7.1	16.2
Mold shrinkage rate　　MD	%	1.59	1.60	1.43	1.01	0.56
TD		1.70	1.72	1.59	1.21	1.78
Centerline average roughness	nm	1.9	2.2	210	430	890

(*1): Because dispersed particles were not lamellar, the ratio, major axis/minor axis, of the dispersed particles was determined.

(*2): Because dispersed particles were not lamellar, the number-average value of the minor axes of the dispersed

particles was determined.

(*3): Because dispersed particles were not lamellar, the maximum value of the minor axis of the dispersed particles was determined.

5

(EXAMPLES 7 to 9)

Polyamide B, the swelling mica obtained in SYNTHETIC EXAMPLE 1 (L-1 and L-2), and electroconductive carbon compound I and electroconductive carbon compound K at the weight ratios 10 set forth in Table 4 were melt-mixed using a twin shaft extruder (TEX 44 produced by Japan Steel Works, Ltd.) while adjusting the temperature to the dies to 230°C to 260°C from the initial stage of the mixing. Evaluation of the resulting polyamide resin compositions was carried out. The results are shown in 15 Table 4.

[0059]

[Table 4]

		EXAMPLES		
		7	8	9
Polyamide B	Parts by weight	100	100	91
Clay L-1		13.6		13.6
Clay L-2			18	
Carbon compound I		4.5	4.5	
Carbon compound K				9
Ash content	wt%	9.9	9.8	10.1
Ratio of [D] ≤ 3,000 Å	%	81	36	80
Average [D]	Å	1420	2830	1410
Number of dispersed particles [N]	no./wt% ·100 μm²	99	45	103
Average aspect ratio	-	106	50	106
Average layer thickness	Å	105	360	105
Maximum layer thickness	Å	510	1650	500
Flexural elastic modulus	MPa	5580	4950	5410
Flexural strength	MPa	116	96	119
Deflection temperature under load	°C	141	131	143
Volume resistivity	Ω·cm	3.7×10^5	5.9×10^5	1.7×10^8
Warpage	mm	1.0	3.6	1.4
Mold shrinkage rate	%			
MD		0.30	0.68	0.44
TD		0.32	0.72	0.50
Centerline average roughness	nm	4.5	7.3	3.5

[Table 6]

		EXAMPLES		
		10	11	12
Polyamide C	Parts by weight	100	100	91
Clay L-1		13.6		13.6
Clay L-2			18	
Carbon compound I		4.5	4.5	
Carbon compound K				9
Ash content	wt%	9.8	9.8	10.1
Ratio of [D] $\leq 3,000$ Å	%	88	37	89
Average [D]	Å	1030	2800	990
Number of dispersed particles [N]	no./wt% ·100 μm^2	130	50	136
Average aspect ratio	-	142	52	145
Average layer thickness	Å	90	350	95
Maximum layer thickness	Å	350	1650	360
Flexural elastic modulus	MPa	5090	4850	5180
Flexural strength	MPa	148	96	150
Deflection temperature under load	°C	188	123	190
Volume resistivity	$\Omega \cdot cm$	2.9×10^5	6.1×10^5	1.8×10^8
Warpage	mm	0.8	3.8	1.3
Mold shrinkage rate	%			
MD		0.35	0.68	0.34
TD		0.45	0.72	0.48
Centerline average roughness	nm	4.0	7.3	3.5

(COMPARATIVE EXAMPLES 11 to 15)

Polyamide C, talc, mica, a glass fiber or electroconductive compound I at the weight ratios set forth in Table 7 were melt-mixed as in EXAMPLE 10 to prepare polyamide resin compositions. Evaluation of the resulting polyamide resin compositions was carried out. The results are shown in Table 7.

[0062]

31

[Table 7]

		COMPARATIVE EXAMPLES				
		11	12	13	14	15
Polyamide C	Parts by weight	100	100	100	100	100
Talc				11		
Mica					11	
Glass fibers						11
Carbon compound I			4.5	4.5	4.5	4.5
Ash content	wt%	0.0	0.0	10.0	10.0	10.0
Ratio of [D] ≤ 3,000 Å	%	Not measured	Not measured	0	0	Not measured
Average [D]	Å	Not measured	Not measured	24200	25800	Not measured
Number of dispersed particles [N]	no./wt%·100 μm²	Not measured	Not measured	5	2	Not measured
Average aspect ratio	-	Not measured	Not measured	1.5 (*1)	1.5 (*1)	Not measured
Average layer thickness	Å	Not measured	Not measured	App. 30,000 (*2)	App. 30,000 (*2)	Not measured
Maximum layer thickness	Å	Not measured	Not measured	App. 900,000 (*3)	App. 900,000 (*3)	Not measured
Flexural elastic modulus	MPa	3200	3200	5150	5400	5810
Flexural strength	MPa	150	150	135	137	140
Deflection temperature under load	°C	130	130	135	139	148
Volume resistivity	Ω·cm	3.3×10^{14}	9.8×10^5	8.3×10^5	3.9×10^5	2.4×10^5
Warpage	mm	4.5	4.5	1.9	2.5	14.7
Mold shrinkage rate MD	%	1.01	1.01	0.54	0.45	0.32
TD		1.11	1.11	0.59	0.49	1.43
Centerline average roughness	nm	1.9	1.9	210	430	790

(*1): Because dispersed particles were not lamellar, the ratio, major axis/minor axis, of the dispersed particles was determined.

(*2): Because dispersed particles were not lamellar, the number-average value of the minor axes of the dispersed particles was determined.

(*3): Because dispersed particles were not lamellar, the maximum value of the minor axis of the dispersed particles was determined.

(EXAMPLES 13 to 15)

Polyamide D, the swelling mica prepared in SYNTHETIC

EXAMPLE 1 (L-1 and L-2), and electroconductive carbon compound I or electroconductive carbon compound K at the weight ratios set forth in Table 8 were melt-mixed using a twin shaft extruder (TEX 44 produced by Japan Steel Works, Ltd.) while adjusting

5   the temperature to the die to 280°C to 300°C from the initial stage of mixing. Evaluation of the resulting polyamide resin compositions was carried out. The results are shown in Table 8.

[0063]

10 [Table 8]

		EXAMPLES		
		13	14	15
Polyamide resin D	Parts by weight	100	100	91
Clay L-1		13.6		13.6
Clay L-2			18	
Carbon compound I		4.5	4.5	
Carbon compound K				9
Ash content	wt%	9.5	9.6	10.1
Ratio of [D] ≤ 3,000 Å	%	103	45	97
Average [D]	Å	1330	2260	1290
Number of dispersed particles [N]	no./wt% ·100 μm^2	123	58	130
Average aspect ratio	-	120	59	133
Average layer thickness	Å	105	330	95
Maximum layer thickness	Å	405	1380	355
Flexural elastic modulus	MPa	7200	5010	7290
Flexural strength	MPa	168	113	170
Deflection temperature under load	°C	118	109	123
Volume resistivity	$\Omega \cdot$cm	4.8×10^5	6.1×10^5	2.8×10^8
Warpage	mm	1.0	3.9	1.2
Mold shrinkage rate	%			
MD		0.45	0.68	0.34
TD		0.54	0.73	0.45
Centerline average roughness	nm	4.2	6.4	3.0

(COMPARATIVE EXAMPLES 16 TO 20)

Using polyamide D, talc, mica, a glass fiber or

35 electroconductive compound K at the weight ratios set forth in

resins decreases the resistivity, but the balance between heat resistance and dimensional stability is not satisfactory. Addition of glass fibers can render heat resistance but causes anisotropic shrinkage, which leads to warpage, low dimensional

5   stability, and low surface quality. The combination of talc and mica can render electric conductivity and dimensional stability but degrades surface quality. Accordingly, it is clear that none of the conventional techniques can provide a conductive material that can achieve satisfactory balance

10   between electric conductivity, mechanical strength, heat resistance, surface quality of the product, mold shrinkage, and dimensional stability such as anisotropy and warpage.

[0065]

[EFFECT OF THE INVENTION]

15   As is described above, the present invention provides polyamide resin composition having a satisfactory balance between properties, such as antistatic properties, superior surface appearance, low warpage due to its low anisotropy, and maintained mechanical properties and heat resistance.

20

[Document Name]   Abstract

[Abstract]

[Problem to be solved by the Invention]   To provide a polyamide resin composition having a satisfactory balance between properties, such as antistatic properties, superior surface appearance, low warpage due to its low anisotropy, and maintained mechanical properties and heat resistance.

[Means for solving problem]

A polyamide resin composition comprising a polyamide resin, swelling mica treated with a polyether compound, and an electroconductive carbon compound shows a satisfactory balance between properties, such as antistatic properties, superior surface appearance, low warpage due to its low anisotropy, and maintained mechanical properties and heat resistance.

[Selective Figure] none